



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US93/04429  <b>(22) International Filing Date:</b> 11 May 1993 (11.05.93)  <b>(30) Priority data:</b> 07/883,974                      15 May 1992 (15.05.92)                      US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> TORGERSON, Peter, Marte ; 4127 U.S. Rt. 35 NW, Washington Ct. House, OH 43160 (US). BALCHU- NAS, Anthony, Thomas ; 5468 Yosemite Drive, Fair- field, OH 45014 (US).		<b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).  <b>(81) Designated States:</b> AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished          upon receipt of that report.</i>
<b>(54) Title:</b> ADHESIVE AGENT CONTAINING POLYSILOXANE-GRAFTED POLYMER, AND COSMETIC COMPOSITIONS THEREOF  <b>(57) Abstract</b>  Polymeric adhesive agents are disclosed which comprise polysiloxane grafted polymers wherein: (a) the polymers are made by polymerization of polysiloxane-containing monomers and non-polysiloxane-containing monomers, typically by free radical polymerization; (b) the adhesive agent has a weight average molecular weight of at least about 20,000 and contains from about 1 % to about 50 %, by weight, of polysiloxane-containing monomer; and (c) the weight percentage of silicon present as unreacted polysiloxane-containing monomer and silicone-grafted polymer having a viscosity at 25 °C of below about 10,000,000 centistokes based on the total silicon present as unreacted silicon monomer and polysiloxane-grafted polymer is about 15 % or less. Also, the adhesive agent contains no more than about 4 %, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25 °C of below about 10,000,000 centistokes. Cosmetic compositions containing such adhesive agents are also disclosed.		

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ADHESIVE AGENT CONTAINING  
POLYSILOXANE-GRAFTED POLYMER, AND  
COSMETIC COMPOSITIONS THEREOF

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TECHNICAL FIELD

The present invention relates to adhesive agents containing polysiloxane-grafted polymers and to compositions, such as cosmetic compositions, containing such adhesive agents. This invention especially relates to adhesive agents useful for hair setting purposes, and to hair setting compositions containing such adhesive agents.

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has recently been discovered that hair care compositions containing polysiloxane-grafted polymers can provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays,

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tonics, lotions, gels, and mousses. The compositions can provide these benefits to hair without leaving the hair stiff or sticky/tacky feel, as do conventional hair setting ingredients.

These types of adhesive, film-forming, polysiloxane-grafted polymers can also be used for other purposes, such as topical application to skin for cosmetic purposes or as a means for delivery of medicaments. The film forming agents can also be used in a wide variety of other adhesive areas, e.g. adhesive paper or binding materials, etc.

Polysiloxane-grafted polymers are disclosed for use in EPO Application 90307528.1, published January 16, 1991 as EPO Publication 0 408 311 A2, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991. Adhesive compositions containing film-forming polysiloxane-grafted polymers are also disclosed in U.S. Patent 4,728,571, issued March 1, 1988, Clemens et al., U.S. Patent 5,021,477, issued June 4, 1991, Garbe et al., U.S. Patent 4,981,902, issued January 1, 1991, Garbe et al., U.S. Patent 4,988,506, issued January 29, 1991, Mitra et al., and U.S. Patent 4,981,903, Mitra et al., issued January 1, 1991, Mitra et al.

Whereas excellent performance can be obtained with these polysiloxane-grafted polymers, particularly for hair setting compositions, it remains desirable to achieve improved adhesive performance. It also remains desirable to achieve higher levels of tactile softness for a given level of adhesion for compositions containing these adhesive agents. In particular, for example, it is desirable to provide hair setting compositions with improved hold and/or higher tactile softness for a given level of hold. It

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is an object of this invention to provide adhesive agents that can provide such enhanced levels of performance.

These and other benefits will become readily apparent from the detailed description which follows.

5 Unless otherwise indicated, all percentages and ratios herein are by weight. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described herein.

#### SUMMARY OF THE INVENTION

10 The present invention relates to a polymeric adhesive agent, especially a film-forming agent, comprising a polysiloxane-grafted polymer made by the polymerization of polymerizable, polysiloxane containing monomers with polymerizable non-polysiloxane-containing monomers, wherein said adhesive agent has a weight average  
15 molecular weight of at least about 20,000, contains from about 1% to about 50%, by weight, of the polysiloxane-containing monomer, and the weight percentage of silicon present as unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers having a viscosity at 25°C of below about 10,000,000 centistokes  
20 based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is about 15% or less. Also, the adhesive agent should contain no more than about 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer  
25 having a viscosity at 25°C of below about 10,000,000.

In another embodiment, the present invention provides cosmetic compositions, especially hair care compositions, eg. hair setting compositions, comprising the adhesive agent hereof and a carrier suitable for application to the hair.

#### 30 DETAILED DESCRIPTION OF THE INVENTION

The essential, as well as various optional, components of the present invention are described below.

##### Polymeric Adhesive Agent

35 The polymeric adhesive agent hereof comprises a film-forming polysiloxane-grafted polymer, made by the polymerization of

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polysiloxane-containing monomers with non-polysiloxane-containing monomers such that said adhesive agent has a weight average molecular weight of at least about 20,000, comprises from about 1% to about 50%, by weight, of the polysiloxane-containing monomers, and the weight percentage of unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers having a viscosity at 25°C of below about 10,000,000 centistokes: to total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is about 15% or less, more preferably about 5% or less. The level of polysiloxane-containing monomers in the adhesive agent, for purposes hereof, includes monomer present in either unreacted (eg., unpolymerized) form as well as monomer incorporated into the adhesive agent in polymer form. Also, the adhesive agent should contain no more than about 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below about 10,000,000, preferably less than about 3% more preferably less than about 2%, most preferably less than about 1%. The limitation pertaining to the adhesive agent sets forth the maximum viscosity level, as described above, can also be limited to is preferably about 1,000,000, about 100,000 or about 10,000, etc.

Cosmetic compositions of the present invention typically contain from about 0.1% to about 10.0%, preferably from about 0.5% to about 8.0%, of the adhesive agent, although higher or lower amounts may be used for particular applications. The adhesive agent hereof can also be used to advantage in other cosmetic products, such as make-up, mascara and eye-liner, nail polish, etc., as well as topical skin products such as creams and lotions, including for delivery of medicaments or other ingredients to the skin. The adhesive agent hereof can further be used for other adhesive applications, such as adhesive paper and backing paper, etc.

The adhesive agent should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the

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invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, especially for cosmetic compositions, the adhesive agents hereof when dried to form a film have a Tg of at least about -20°C, preferably at least about 20°C, so that they are not sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer. Preferably, the Tm, if any, is also above about -20°C, more preferably above about 20°C.

The polymers useful in the compositions of the present invention are polysiloxane-grafted polymers of polymerizable "silicone-containing", or "polysiloxane-containing", monomers with non-silicone-containing monomers. The polysiloxane-grafted polymers should satisfy the following four criteria:

- (1) when dried the polymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently grafted to the non-silicone portion; and
- (3) the molecular weight of the silicone portion is at least about 500; and

When used in a composition, such as a cosmetic composition for application to the hair or skin, the non-silicone portion should render the entire polymer soluble or dispersible in the composition vehicle and permit the polymer to deposit on the intended surface, eg. hair or skin.

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The most preferred polymers comprise an organic backbone, especially a carbon backbone such as a vinyl polymeric backbone, and also preferably, a polydimethylsiloxane macromer having a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000, is grafted to the backbone. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers. These include vinyl monomers, and other condensation monomers (eg., those that polymerize to form polyamides and polyesters) and ring-opening monomers (eg., ethyl oxazoline and caprolactone). The polymer is such that when it is formulated into the finished composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer which results in the desired combination of tactile feel and setting, film-forming, or adhesive benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the



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concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface with the silicone oriented at the surface of the film. This can be demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These polymers are comprised of: at least one free radically polymerizable vinyl monomer or monomers (A); and optionally at least one reinforcing monomer copolymerizable with A which is more hydrophilic than A and is selected from the group consisting of hydrophilic monomers and macromers having a Tg or a Tm above about -20°C (B). The polymers also comprise polysiloxane-containing monomers. (C) Polymerizable macromers which can be used herein shall be referred to herein collectively with polymerizable monomers as "monomers", for convenience. Hydrophobic monomers means monomers which form substantially water insoluble homopolymers. Hydrophilic monomers means monomers which do not form substantially water insoluble homopolymers. Suitable polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed

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August 27, 1991, all of which are incorporated by reference herein.

5 The polysiloxane-grafted polymers hereof comprise from about 1% to about 50%, by weight of C monomers, i.e., the polysiloxane-containing monomers, and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers, which can be monomers selected from the group consisting of A and B monomers, and mixtures thereof.

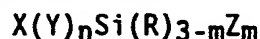
10 Representative examples of hydrophobic, A monomers are acrylic or methacrylic acid esters of  $C_1$ - $C_{18}$  alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 15 t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include 20 n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof. Most preferably, A is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

25 Representative examples of hydrophilic, B monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, 30 diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers

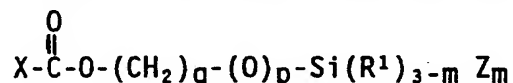
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(such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.

The preferred polymerizable polysiloxane-containing monomer (C monomer) can be exemplified by the general formula:



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C<sub>1</sub>-C<sub>4</sub>), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight as described above. Preferably, the C monomer has a formula selected from the following group:



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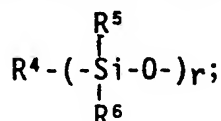
In this structure, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; R<sup>1</sup> is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl (preferably R<sup>4</sup> is alkyl); X is

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R<sup>2</sup> is hydrogen or -COOH (preferably R<sup>2</sup> is hydrogen); R<sup>3</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH (preferably R<sup>3</sup> is methyl); Z is

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5 R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> independently are lower alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen or hydroxyl (preferably R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are alkyls); and r is an integer of about 5 or higher, preferably about 10 to about 1500 (most preferably r is from about 100 to about 250). Most preferably, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are methyl, p=0, and q=3.

10 In general, the total of A and B monomers in the adhesive agent polymer will preferably be from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95)%, by weight of the polymer of the adhesive agent. The level of A monomers can be from 0% to about 99%; the level of B monomers, from 0% to about 99%; and the level of C monomers, from 1% to about 50%, preferably from about 1% to about 40%, more preferably from about 2% to about 25%, of monomer C. The  
15 composition of any particular adhesive agent polymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the adhesive agent polymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous  
20 formulation or other polar or hydrophilic solvents preferably have from about 0% to about 85% (preferably from about 5% to about 70%) monomer A, from about 14% to about 95% (preferably from about 29% to about 80%) monomer B, and from about 1% to about 40% (preferably from about 2% to about 25%) monomer C. Polymers which  
25 are dispersible in aqueous formulations have the preferred composition: from about 0% to about 70% (preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% (preferably from about 2% to about 25%) monomer C. Polymers  
30 which are soluble or dispersible in less polar or nonpolar solvents, such as cyclomethicone, preferably comprise from about 5% to about 98% (preferably from about 50% to about 90%) of monomer A, from 0 to about 80% (preferably from 0% to about 45%, most preferably from 0% to about 20% of monomer B, and from about

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1% to about 40% (preferably from about 2% to about 25%) of monomer C.

5 The polysiloxane-grafted polymers can be synthesized as follows. In general, the polymers can be made by free radical polymerization of silicone- or polysiloxane-containing monomers with non-silicone- or non-polysiloxane-containing monomers. The  
10 filming forming, cosmetic agent comprising this product is prepared by substantially removing the unreacted polysiloxane-containing monomers and polysiloxane-grafted polymers which have a fluid viscosity at 25°C of below about 10,000,000, to the levels defined by silicon present as described above. The monomer and polymeric material removed are both of relatively low molecular weight, compared to the molecular weight of the cosmetic agent hereof.

15 It is not intended to necessarily exclude from this invention any polysiloxane-grafted polymer made by free radical polymerization or by means other than free radical polymerization, so long as the product is substantially free of the above-mentioned, undesired materials, either by means of  
20 purification subsequent to reaction or as a result of an improved reaction or different type of synthesis. However, it is to be understood that block copolymers of alternating organic block and silicone blocks are not included as polysiloxane-grafted polymers.

25 The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable.  
30 Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur,  
35 assuming thermal initiators are used. Alternatively, redox or

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radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified, as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 20 parts acrylic acid, 60 parts t-butylacrylate, and 20 parts polysiloxane (10,000 MW)-containing monomer in a flask. Add sufficient ethyl acetate or acetone (preferably acetone) as the reaction solvent to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the reaction solvent by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven. A similar procedure can be used to make an 80%/120% t-butyl acrylate/polysiloxane (10,000 MW)-containing monomer. Ethyl acetate is the preferred solvent for this synthesis.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62°C in a water bath. Add

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initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Maintain temperature at 62°C, with a sufficient rate of argon flow to keep the solution mixed. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

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10 Polymer III: Place 10.5 parts N,N-dimethylmethacrylamide, 56 parts isobutyl methacrylate, 3.5 parts 2-ethylhexylmethacrylate, and 30 parts 10K PDMS macromer in a reaction vessel fitted with an argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene or isopropanol to bring the final monomer concentration to 20% by weight. Begin stirring and sparge with argon for 1 hour. While sparging, heat to 60°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% (if toluene is the solvent) or 0.125% (if isopropanol is the solvent) by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60°C. Allow to react for 6 hours. Terminate the reaction and remove the solvent as with Polymer II.

15  
20 Removal of unwanted polysiloxane-containing monomer and/or polysiloxane-grafted polymeric material that has viscosity below 10,000,000 at 25°C from free radically polymerized product can be done by any means known in the art. The materials to be removed, in general, will be of lower molecular weight than the average molecular weight of the polymer material prior to extraction. Also, such materials to be removed will contain a relatively high proportion of polysiloxane relative to the organic component-generally, although not necessarily, in excess of 50% polysiloxane.

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Techniques suitable for removing the unwanted material include a variety of standard procedures known in the art.

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One method that can be used is supercritical fluid extraction, such as with supercritical carbon dioxide.

Supercritical fluid extraction is carried out on polymer which has been dried from the original reaction mixture to remove excess reaction solvent. Dried polymer is preferably ground to create a fine powder, which allows for increased surface area and maximum extraction efficiency. Extraction can be carried out using supercritical carbon dioxide in conventional extractors suitable for supercritical fluid extraction. The extraction should be conducted at a temperature of at least about 40 deg C and a pressure of between about 400-600 atmospheres. The particular temperature and pressure will depend upon criteria well known in the art, such as specific solvent, polymer sample size, fineness of the ground material, and the desired extraction efficiency. Extraction occurs via continuous purging under pressure with supercritical carbon dioxide, typically over a period of about 1-4 hours. Unreacted polysiloxane-containing monomer and low molecular weight polysiloxane-containing polymer is solubilized by carbon dioxide and is then transported away from the remaining polymer via standard procedures, e.g., by a transfer line.

Another generally applicable method is membrane separation, performed in accordance with standard techniques known in the art.

A method which can be useful, particularly for adhesive agents utilizing polysiloxane-grafted polymers that are soluble in water, alcohol, or other polar solvents, is solvent extraction with a nonpolar solvent. Suitable solvents include C<sub>3</sub>-C<sub>8</sub> hydrocarbons, preferably C<sub>5</sub> -C<sub>6</sub> hydrocarbons, such as hexane. Before performing the extraction, the polymer reaction product is precipitated out of the reaction solvent (e.g., with water), and dried. The extraction solvent is preferably heated to near or slightly above the average T<sub>g</sub> of the non-silicone backbone portion of the polysiloxane-grafted polymer of the adhesive agent. The temperature should be high enough so that the polymer softens, but not so high such that it congeals. The T<sub>g</sub> of the polymer will



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vary from species to species of polymer. The extraction solvent and reaction product can be mixed before, or after heating the solvent. The extraction solvent and polymer reaction product should be held with mixing and preferably in an excess of solvent, for a reasonable period to effectuate removal of the soluble materials. This period will depend upon the reflux temperature of the solvent, the T<sub>g</sub> of the polysiloxane-grafted polymer of the adhesive agent, the temperature to which the solvent is actually heated, the desired level of removal of unreacted monomer and the polysiloxane-containing polymer having viscosity at 25°C below about 10,000,000, and the number of cycles of solvent extraction to be performed. Typically, the solvent extraction periods will be from about one-half hour to about two hours, more typically from about one-half hour to about one hour. The solvent can be removed after each cycle by conventional means, e.g., decanting, filtering, etc., with drying or distillation to remove trace extraction solvent remaining in the product after the final extraction cycle.

Analysis of the polymer reaction product and the extracted materials, and the purified film-forming agent can be done by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resource (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, and atomic absorption and emission spectroscopies.

25

#### Carrier

The cosmetic compositions of the invention comprise the a carrier, or a mixture of such carriers, which are suitable for application to skin or hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%; most preferably from about 10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate solvent will also depend on the particular polymer

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to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

5 The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone-grafted polymer being used. The  
10 silicone-grafted polymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (e.g. C<sub>1</sub>-C<sub>6</sub> monohydric alcohols, such as ethanol and isopropanol), hydro-  
15 alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), lin-  
lcool, hydrocarbon esters (such as ethyl acetate, dibutyl phtha-  
late), volatile silicon derivatives, especially siloxanes (such as  
phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclo-  
tetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl  
20 pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl  
cyclopentasiloxane, cyclomethicone, and dimethicone (having for  
example, viscosity at 25°C of about 15 centipoise or less), and  
mixtures thereof. Preferred solvents include water, ethanol,  
volatile silicone derivatives, and mixtures thereof. The solvents  
25 used in such mixtures may be miscible or immiscible with each  
other.

Where the cosmetic compositions are conditioner compositions, such as hair rinses or skin conditioners the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant  
30 vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science  
35 82-91 (1968); Barry, et al., "The Self-Bodying Action of

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Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The carrier may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle

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material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred carrier for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al, and U.S. Patent 5,100,657, issued March 31, 1992 to Ansher-Jackson et al., each incorporated herein by reference.

Carriers, suitable for use with the present invention include, for example, those used in the formulation of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilize an emulsifying agent. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are especially preferred, particularly if the product is a hair spray composition and most especially if it is a spray composition having relatively low levels of volatile organic solvents, such as alcohols, and relatively high levels of water (e.g., in excess of about 10%, by weight water). If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

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Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or can having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

#### Optional Ingredients

The cosmetic compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

#### Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials typically have the respective formulae  $\text{ROSO}_3\text{M}$  and

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$RO(C_2H_4O)_xSO_3M$ , wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine.

5 Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



10 wherein  $R_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having  
15 carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $C_{12-18}$  n-paraffins.

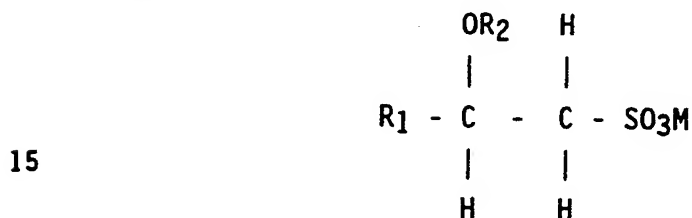
20 Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for  
25 example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

30 Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

35 Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The

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term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of  $\alpha$ -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



where  $\text{R}_1$  is a straight chain alkyl group having from about 6 to about 20 carbon atoms,  $\text{R}_2$  is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

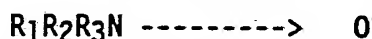
Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

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2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products.

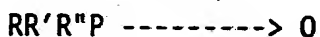
3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides such as those corresponding to the following general formula:



wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula is a conventional representation of a semipolar bond).

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein  $R$  contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

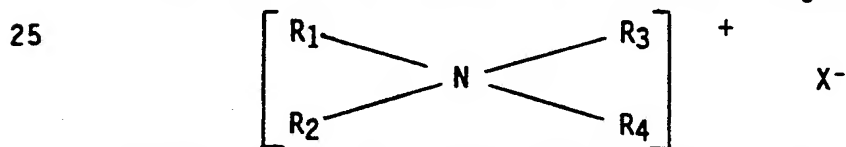


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Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9,-trixaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein  $R_1$ - $R_4$  are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino

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groups. The longer chain aliphatic groups, eg., those of about 12 carbons, or higher, can be saturated or unsaturated.

Other quaternary ammonium salts useful herein are diquaternary ammonium salts, such as tallow propane diammonium dichloride.

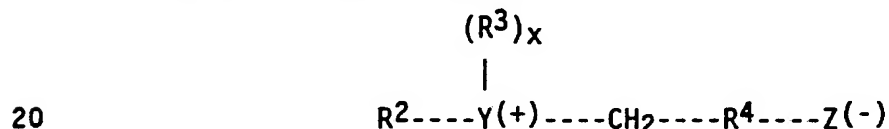
Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R<sub>1</sub> and R<sub>2</sub> have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(saturated or unsaturated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable

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amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055; Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl

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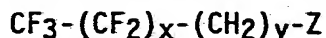
bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by  
5 coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the  $RCONH(CH_2)_3$  radical is attached to the nitrogen atom of the betaine are also useful in this  
10 invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched  
15 chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylamino-  
20 propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.  
25

#### Fluorosurfactant

The compositions of the present invention can contain, fluorosurfactant. Suitable fluorosurfactant can be cationic, anionic, amphoteric, zwitterionic, nonionic or a mixture thereof.

30 Fluorosurfactants include perfluorinated compounds such as those represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to  
35 17, particularly from 7 to 11, and y is an integer from 0 to 4,

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and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

Cationic fluorosurfactants include fluorinated alkyl quaternary ammonium salts having a variety of anionic counterions, including iodide, chloride, methosulfate, phosphate, and nitrate salts, preferably an iodide; and those fluorosurfactants conforming to the formula  $R_fCH_2CH_2SCH_2CH_2N^+(CH_3)_3[CH_3SO_4]^-$  wherein  $R_f = F(CF_2CF_2)_{3-8}$ , such as Zonyl FSC® supplied by DuPont. Preferred fluorinated alkyl quaternary ammonium iodides are supplied under the tradename Fluorad FC-135® supplied by 3M.

Anionic fluorosurfactants include mono-, and bis-perfluoroalkyl phosphates, such as Zonyl FSP® supplied by DuPont and conforming to the general formulae  $(R_fCH_2CH_2O)P(O)(ONH_4)_2$   $(R_fCH_2CH_2O)_2P(O)(ONH_4)$  wherein  $R_f = F(CF_2CF_2)_{3-8}$ ; mono- and bis-fluoroalkyl phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, complexed with non-fluorinated quats, preferably aliphatic quaternary methosulfates, such as Zonyl FSJ® supplied by DuPont; perfluoroalkyl sulfonic acid having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, such as Zonyl TBS® supplied by DuPont and conforming to the formula  $R_fCH_2CH_2SO_3X$  wherein  $R_f = F(CF_2CF_2)_{3-8}$  and  $X = H$  and  $NH_4$ ; telomer phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably diethanolamine salts, such as Zonyl RP® supplied by DuPont; amine

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perfluoroalkyl sulfonates, such as Fluorad FC-99<sup>®</sup> supplied by 3M; ammonium perfluoroalkyl sulfonates, such as Fluorad FC-93<sup>®</sup>, Fluorad FC-120<sup>®</sup> and L-12402<sup>®</sup>, supplied by 3M; potassium perfluoroalkyl sulfonates, such as Fluorad FC-95<sup>®</sup> and Fluorad FC-98<sup>®</sup> supplied by 3M; potassium fluorinated alkyl carboxylates, such as Fluorad FC-129<sup>®</sup> supplied by 3M; ammonium perfluoroalkyl carboxylates, such as Fluorad FC-143<sup>®</sup> supplied by 3M; and those fluorosurfactants conforming to the general formula  $R_fCH_2CH_2SCH_2CH_2CO_2Li$  wherein  $R_f=F(CF_2CF_2)_{3-8}$ , such as Zonyl FSA<sup>®</sup> supplied by DuPont.

Amphoteric fluorosurfactants include fluorinated alkyl amphoteric such as Fluorad FC-100<sup>®</sup> supplied by 3M.

Zwitterionic fluorosurfactants preferred for use in the present compositions are those fluorosurfactants conforming to the formula  $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$  wherein  $R_f=F(CF_2CF_2)_{3-8}$  such as Zonyl FSK<sup>®</sup> supplied by DuPont.

Fluorosurfactants can be used alone or in combination in the hair spray compositions of the present invention.

Fluorosurfactants, when used, will typically be present at from about 0.01% to about 2%, preferably from about 0.01% to about 1.5%, by weight of the composition.

The above-mentioned surfactants can be used alone or in combination in the compositions hereof.

The cosmetic compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium

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sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as  
5 any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin, disobutyl adipate,  
10 butyl stearate, and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions generally will be between  
15 about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The cosmetic compositions of the present invention can be  
20 made using conventional formulation and mixing techniques. Methods of making various types of cosmetic compositions are described more specifically in the following examples.

#### Method of Use

The cosmetic compositions of the present invention are used  
25 in conventional ways to provide the conditioning/styling/hold/adhesive/film-forming or other benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair or skin, which may  
30 then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, skin lotion, film-forming skin lotion with medicament, and tonic products). By "effective amount" is meant an amount sufficient to provide the film-forming  
35 benefits desired. Preferably, hair rinse, mousse, and gel

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products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already  
5 been dried and styled. Cosmetics and skin lotions are applied to face, skin, or eye area in the conventional manners of usage for those types of products.

In another aspect hereof, adhesive agents containing polysiloxane-grafted polymers, such as those described in U.S.  
10 Patent 4,693,935, Mazurek, issued September 15, 1987 and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, can be used in adhesive products such as adhesive tapes and backing sheets for adhesive materials. Thus, the adhesive agents hereof also can include non-pressure sensitive as well as pressure sensitive  
15 film-forming polymers.

The following experimentals and examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as  
20 many variations of the invention are possible without departing from its spirit and scope.

#### Experimental A

A 60%/20%/20% t-butyl acrylate/acrylic acid/polydimethylsiloxane-containing (PDMS) vinyl monomer (10,000 MW) is made by  
25 free radical polymerization in an acetone reaction medium, as described above for Polymer I. The percentages represent the weight percent of the total monomer added to the reaction.

The reaction product is precipitated out of the acetone by water addition and dried. Hexane extraction of the reaction  
30 product is then performed by adding an excess of hexane to the reaction product and heating to reflux, about 70°C. The Tg of the non-silicone portion of the adhesive agent polymer is about 63°C. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by  
35 vacuum suction. Two more hexane extraction cycles are conducted



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in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

#### Experimental B

5 An 80%/20% t-butyl acrylate PDMS (10,000 MW) polymer is made according to the same procedures as for Polymer I, above, except that the monomers that are polymerized are 80%, by weight, t-butyl acrylate and 20%, by weight, of the PDMS-containing vinyl monomer. The reaction medium is ethyl acetate.

10 The reaction product is precipitated out of the reaction solvent by water addition and dried. The polymer is next ground to a fine powder in preparation for supercritical fluid extraction with carbon dioxide. The extraction is carried out at a temperature of about 40°C and a pressure of about 600 atmospheres. 15 The extraction vessel is continuously purged under pressure with supercritical carbon dioxide over a period of about 1 hour.

Low molecular weight polysiloxane-containing monomer and polymer about 1 hour is solubilized by the supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurized and dry, extracted polymer is recovered from the extraction vessel.

#### 25 EXAMPLES I-III

The following are hair spray compositions representative of the present invention.

<u>Component</u>	<u>Example # (Weight %)</u>		
	<u>I</u>	<u>II</u>	<u>III</u>
30 Polysiloxane-Grafted Polymer (Exp. A)	4.5	4.5	4.5
Ethanol	79.0	79.0	86.4
Diisobutyl adipate	0.7	--	--
Potassium Hydroxide Solution (45% conc)	1.0	1.0	1.0
Perfume	0.2	0.2	0.2
FC-120 Fluorosurfactant (3M Co)(25% active)	--	--	0.14
Water	q.s. to 100%		

35 This product is prepared by dissolving the silicone polymer to the ethanol and mixing for several hours until all the polymer

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is dissolved. Plasticizer is then added, if applicable. Potassium hydroxide is then added. Water or water/surfactant, as applicable, is added. Fragrance is added last. All ingredients are added under mixing conditions. The product can be packaged in conventional nonaerosol pump spray containers and compressed air pump spray aerosol containers.

#### EXAMPLE IV

The following is a hair grooming tonic composition representative of the present invention.

Component	Weight %
Polysiloxane-Grafted Polymer (Exp. A)	0.70
Perfume	0.10
Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

#### EXAMPLE V

The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Polysiloxane-Grafted Polymer (Exp. A)	2.00
Ethanol	10.00
PEG 150 distearate	2.00
NaOH	0.15
Glydant <sup>1</sup>	0.38
Perfume	1.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient

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temperature. Composition pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

EXAMPLE VI

5 The following is a cold-wave hair perm composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Thioglycolic acid	5.00
	Monoethanolamine	6.00
	Polysiloxane-Grafted Polymer (Exp. A)	1.50
10	PEG 10 monostearate	0.50
	DRO H <sub>2</sub> O	q.s.

The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60°C and then cooling to ambient temperature.

15 EXAMPLE VII

The following is a styling gel composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted Polymer (Exp. A)	2.00
20	Carbopol 940 <sup>1</sup>	0.75
	Triethanolamine	1.00
	Dye solution	0.05
	Perfume	0.10
	Laureth-23	0.10
25	DRO H <sub>2</sub> O	q.s.

<sup>1</sup> cross-linked polyacrylic acid, commercially available from B. F. Goodrich

This batch is made by mixing the listed components together in a conventional manner.

30 EXAMPLE VIII

The following is a hair mousse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted Polymer (Exp. A)	3.00
35	Ethanol	15.00

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	Cocamine oxide	0.60
	D.C. 190 <sup>1</sup>	0.20
	Cocamide DEA	0.30
	Perfume	0.10
5	Isobutane	7.00
	DRO H <sub>2</sub> O	q.s.

<sup>1</sup> dimethicone copolyol, commercially available from Dow Corning

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

#### Examples IX-X

The following are hair styling/conditioning rinse compositions representative of the present invention.

	<u>Composition</u>	<u>IX</u>	<u>X</u>
	Citric Acid	0.02	0.02
	Sodium Citrate	0.09	0.09
	Cetyl Alcohol	0.12	0.12
20	Stearyl Alcohol	0.08	0.08
	Natrosol Plus CS Grade D-67 <sup>1</sup>	1.05	1.10
	Xanthan Gum <sup>2</sup>	0.25	0.25
	Styling Polymer Premix		
	Polysiloxane-Grafted Polymer (Exp. B)	1.75	1.75
25	Octamethyl cyclotetrasiloxane	5.98	5.98
	Decamethyl cyclopentasiloxane	2.56	2.56
	Butyl Stearate	0.15	0.15
	Kathon CG	0.03	0.03
	Perfume	0.33	0.33
30	Conditioner Premix		
	DRO Water	12.18	11.88
	Adogen 442-100P <sup>4</sup>	0.75	0.75
	Adogen 471 <sup>5</sup>	--	0.60
	Stearyl Trimethyl		
35	Ammonium Chloride	0.30	--

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## Silicone Gum Premix

	Decamethyl cyclopentasiloxane	1.42	1.42
	Polydimethyl Siloxane Gum <sup>3</sup>	0.25	0.25
	Amodimethicone (Dow Corning Q2-8220)	--	0.10
5	DRO Water	q.s.	q.s.

<sup>1</sup>Hydrophobically modified hydroxyethyl cellulose from Aqualon Corp.

<sup>2</sup>Readily dispersible xantham gum

10 <sup>3</sup>SE-76 gum available From General Electric

<sup>4</sup>Ditallow dimethyl ammonium chloride, Sherex Chemical Co., Dublin, Ohio, USA.

<sup>5</sup>Tallow trimethyl ammonium chloride, Sherex Chemical Co.

15 The styling polymer premix is prepared by combining the polymer, the octamethyl tetrasiloxane and decamethyl pentasiloxane, and butyl stearate.

The silicone gum premix is prepared by combining and mixing (in a separate vessel) the silicone gum and decamethyl cyclopentasiloxane until homogeneous.

20 The conditioner premix is prepared by combining and mixing (in a separate vessel) DRO water, any primary and secondary thickeners (premelted if necessary to ensure homogeneity) at 82° the silicone gum premix, and amodimethicone at 71°C, until homogeneous.

25 In another vessel, the DRO water is heated to 71°C. Citric acid, sodium citrate, cetyl alcohol, stearyl alcohol and Natrosol Plus CS grade D-67 are added and mixed until homogeneous. The xanthan gum is added and mixed until homogeneous. The styling polymer premix, Kathon CG and perfume are added and mixed until  
30 homogeneous. The composition is further dispersed with an in-line homogenizer (such as Tekmar homogenizer) and then cooled to 38°C.

The conditioner premix is also further dispersed with an in-line homogenizer and cooled to 38°C and added to the final vessel, mixing until homogeneous to form the styling rinse  
35 composition.

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When the compositions defined in Examples I-X are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

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EXAMPLE XI

An aerosol hair spray composition of the present invention is prepared as follows:

	<u>Component</u>	<u>Weight %</u>
	Polysiloxane-Grafted	4.00
10	Polymer (Exp. A)	
	Water	11.00
	Ethanol	63.50
	KOH (45% solution)	0.90
	Isobutane	15.00
15	Difluoroethane	6.00

All of the ingredients except for the propellants are mixed together at ambient temperature until the polymer is dissolved. The mixture is placed in an aerosol can which is then equipped with a conventional aerosol spray can valve, which is vacuum crimped in place. The propellants are then filled through the valve and the can is equipped with a conventional aerosol spray can activator.

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## WHAT IS CLAIMED IS:

1. A polymeric adhesive agent comprising a polysiloxane-grafted polymer, made by the polymerization of polysiloxane-containing monomers with non-polysiloxane-containing monomers, wherein said adhesive agent has a weight average molecular weight of at least 20,000 and contains from 1% to 50%, by weight, of polysiloxane-containing monomers, characterized in that said adhesive agent: has a weight percentage of silicon present as unreacted polysiloxane-containing monomer and polysiloxane grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer of 15% or less; and contains no more than 4%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes.

2. An adhesive agent as in Claim 1, wherein the weight percentage of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymers having a viscosity at 25°C of below 10,000,000 centistokes based on the total silicon present as unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer is 10% or less, preferably 5% or less, and said adhesive agent contains no more than 3%, preferably no more than 1%, by weight, of unreacted polysiloxane-containing monomer and polysiloxane-grafted polymer having a viscosity at 25°C of below 10,000,000 centistokes.

3. An adhesive agent as in Claim 1 or 2, wherein said weight average molecular weight of said adhesive agent is at least 75,000, preferably at least 100,000, more preferably from 100,000 to 750,000.

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4. An adhesive agent as in Claim 1, 2, or 3, wherein said polymer comprises from 50% to 99%, by weight of the adhesive agent, of polymerizable, ethylenically unsaturated polymerizable monomers, and from 1% to 50% preferably from 2% to 25% of polysiloxane-containing monomers having a molecular weight of at least 1,000 and the general formula:

$X(Y)_nSi(R)_{3-m}(Z)_m$  wherein

X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, hydroxyl, lower alkyl, aryl, alkaryl, alkylamino, or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization

n is 0 or 1, and

m is an integer from 1 to 3.

5. An adhesive agent as in Claim 4, wherein said non-polysiloxane-containing monomer is a free radically polymerizable vinyl .

6. An adhesive agent as in Claim 4 or 5, wherein said non-polysiloxane-containing monomers are selected from the group consisting of hydrophobic monomers selected from the group consisting of acrylic acid esters of  $C_1$ - $C_{18}$  alcohols, methacrylic acid esters of  $C_1$ - $C_{18}$  alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene propylene, vinyl toluene, acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide,



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N-t-butyl acrylamide, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof, and hydrophilic monomers selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, salts of the above acids and amines, and mixtures thereof.

7. An adhesive agent as in Claim 6, wherein said hydrophobic monomers are selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

8. An adhesive agent as in Claim 6 or 7, wherein said hydrophilic monomers are selected from the group consisting of acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, salts of the above acids and amines, and mixtures thereof.

9. An adhesive agent as in Claim 6, 7, or 8, comprising from 0% to 85%, by weight, of said hydrophobic monomers, from 14% to 95% of said hydrophilic monomers, and from 1% to 40% of said polysiloxane-containing monomers, preferably from 5% to 70% of said hydrophobic monomers, from 29% to 80% of said

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hydrophilic monomers, and from 2% to 25% of said polysiloxane-containing monomers.

10. An adhesive agent as in Claim 6, 7, or 8, comprising from 0% to 70%, by weight, of said hydrophobic monomers, from 20% to 80% of said hydrophilic monomers, and from 1% to 40% of said polysiloxane-containing monomers, preferably from 5% to 70% of said hydrophobic monomers, from 20% to 60% of said hydrophilic monomers, and from 2% to 25% of said polysiloxane-containing monomers.

11. A hair care composition useful for styling hair, comprising the adhesive agent of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 and a carrier suitable for application to the hair.

12. A hair care composition as in Claim 11, in the form of liquid suitable for spray application to the hair, wherein said carrier comprises water, C<sub>1</sub>-C<sub>6</sub> monohydric alcohol, or a mixture thereof.